

CLAIMS

What is claimed is:

1. A vulcanizate comprising:

5 a vulcanized rubber formulation comprising at least one vulcanized rubber and a filler, where the at least one vulcanized rubber includes a vulcanizate of a sequentially functionalized polymer that is prepared by reacting an anionically polymerized living polymer with a functionalizing agent X' to produce an end-functionalized polymer that will
10 react or interact with carbon black, silica, or both and that comprises a reactive electrophilic or nucleophilic site; and reacting the reactive site with a functionalizing agent Y' to produce a sequentially functionalized polymer that will react or interact with carbon black and silica.

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2. The vulcanizate of claim 1, where the anionically polymerized living polymer is a copolymer of styrene and 1,3-butadiene.

3. The vulcanizate of claim 1, where X' comprises 1,3-dimethylimidazolidinone, N-methylpyrrolidinone, dicyclohexylcarbodiimide, benzonitrile, a substituted
20 nitrile, a substituted aziridine, a thiazoline, a dialkylaminobenzaldehyde, a bis(dialkylamino)benzophenone, a substituted epoxy compound, N-methylcaprolactam, a substituted Schiff base, a substituted styrylmethyl derivative, vinyl pyridine, a short block of polyvinylpyridine, a polysulfoxide, a
25 poly(carbodiimide), a poly(meth)acrylamide, a poly(aminoalkyl(meth)acrylate), polyacrylonitrile, polyethylene oxide, butyl glycidyl ether, monoglycidyl siloxane, polysiloxane with epoxide endgroups, diphenyl ethylene, or a functionalized styrene.

30 4. The vulcanizate of claim 1, where X' comprises 1,3-dimethylimidazolidinone, 3-glycidoxypropyltrimethoxysilane, N-methylpyrrolidinone, or monoglycidyl ether terminated poly(dimethylsiloxane).

5. The vulcanizate of claim 1, where Y' comprises a silane, alkoxy silane, alkoxy alkyl silane, alkoxy halo alkyl silane, epoxy-generating reagent, substituted acid chloride, substituted isocyanate, substituted benzylic halide, substituted allylic halide, substituted α,β -unsaturated ketone, α,β -unsaturated ester, α,β -unsaturated amide, or bis(dialkylamino)phosphoryl chloride.

6. The vulcanizate of claim 1, where Y' comprises gamma-isocyanatopropyl-triethoxysilane, gamma-isothiocyanatopropyl-triethoxysilane, gamma-isocyanatopropyl-trimethoxysilane, gamma-isothiocyanatopropyl-trimethoxysilane epichlorohydrin, epibromohydrin, triethoxysilyl propyl chloride, diethoxymethylsilyl propyl chloride, and diethylcarbamyl chloride, 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane, or a multi-epoxidized, high-vinyl, poly- or oligo-butadiene or a poly- or oligo-isoprene.

7. The vulcanizate of claim 1, where Y' comprises a short-chain polymer group.

8. The vulcanizate of claim 1, where the filler includes carbon black, silica, or a mixture thereof.

9. The vulcanizate of claim 1, where the vulcanizate further includes a vulcanized natural rubber or vulcanized synthetic rubber other than the sequentially functionalized polymer.

10. A method for preparing a sequentially functionalized polymer, the method comprising:

reacting an anionically polymerized living polymer with a functionalizing agent X' to produce an end-functionalized polymer that will react or interact with carbon black, silica, or both and that comprises a reactive electrophilic or nucleophilic site; and

reacting the reactive site with a functionalizing agent Y' to produce a sequentially functionalized polymer that will react or interact with carbon black and silica.

11. The method of claim 10, where the anionically polymerized living polymer is a copolymer of styrene and 1,3-butadiene.

12. The method of claim 10, where X' comprises 1,3-dimethylimidazolidinone, N-methylpyrrolidinone, dicyclohexylcarbodiimide, benzonitrile, a substituted nitrile, a substituted aziridine, a thiazoline, a dialkylaminobenzaldehyde, a bis(dialkylamino)benzophenone, a substituted epoxy compound, N-methylcaprolactam, a substituted Schiff base, a substituted styrylmethyl derivative, vinyl pyridine, a short block of polyvinylpyridine, a polysulfoxide, a poly(carbodiimide), a poly(meth)acrylamide, a poly(aminoalkyl(meth)acrylate), polyacrylonitrile, polyethylene oxide, butyl glycidyl ether, monoglycidyl siloxane, polysiloxane with epoxide endgroups, diphenyl ethylene, or a functionalized styrene.

13. The method of claim 10, where X' comprises 1,3-dimethylimidazolidinone, 3-glycidoxypropyltrimethoxysilane, N-methylpyrrolidinone, or monoglycidyl ether terminated poly(dimethylsiloxane).

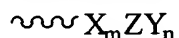
14. The method of claim 10, where Y' comprises a silane, alkoxy silane, alkoxy alkyl silane, alkoxy halo alkyl silane, epoxy-generating reagent, substituted acid chloride, substituted isocyanate, substituted benzylic halide, substituted allylic halide, substituted α,β -unsaturated ketone, α,β -unsaturated ester, α,β -unsaturated amide, or bis(dialkylamino)phosphoryl chloride.

15. The method of claim 10, where Y' comprises gamma-isocyanatopropyl-triethoxysilane, gamma-isothiocyanatopropyl-triethoxysilane, gamma-isocyanatopropyl-trimethoxysilane, gamma-isothiocyanatopropyl-trimethoxysilane epichlorohydrin, epibromohydrin, triethoxysilyl propyl chloride, diethoxymethylsilyl propyl chloride, and diethylcarbonyl chloride, 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane, or a multi-epoxidized, high-vinyl, poly- or oligo-butadiene or a poly- or oligo-isoprene.

16. The method of claim 10, where Y' comprises a short-chain polymer group.

17. The method of claim 10, further comprising the step of reacting the reactive site with a chain-extending group Z to form a chain-extended functionalized polymer that comprises a reactive electrophilic or nucleophilic site.

- 5 18. A functionalized polymer defined by the formula



where $\sim\sim\sim$ is an anionically polymerized polymer segment, X comprises a first functional group that will react or interact with carbon black, silica, or both, Y comprises a second functional group that will react or interact with carbon black, silica, or both, Z is a bond or a chain-extending group, and m and n are each
10 integers from 1 to about 50, with the proviso that when X will react or interact with carbon black but not with silica, Y will react or interact with silica, and when X will react or interact with silica but not with carbon black, Y will react or interact with carbon black.